



The mechanism of halogen liberation in the polar troposphere

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**The mechanism of
halogen liberation in
the polar troposphere**

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The mechanism of halogen liberation in the polar troposphere

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Abstract

Sudden depletions of tropospheric ozone during spring were reported from the Arctic and also from Antarctic coastal sites. Field studies showed that those depletion events are caused by reactive halogen species, especially bromine compounds. However the source and seasonal variation of reactive halogen species is still not completely understood. There are several indications that the halogen mobilisation from the sea ice surface of the polar oceans may be the most important source for the necessary halogens. Here we present a 1-D model study aimed at determining the primary source of reactive halogens. The model includes gas phase and heterogeneous bromine and chlorine chemistry as well as vertical transport between the surface and the top of the boundary layer. The autocatalytic Br release by photochemical processes (bromine explosion) and subsequent rapid bromine catalysed ozone depletion is well reproduced in the model and the major source of reactive bromine appears to be the sea ice surface. The sea salt aerosol alone is not sufficient to yield the high levels of reactive bromine in the gas phase necessary for fast ozone depletion. However, the aerosol efficiently 'recycles' less reactive bromine species (e.g. HBr) and feeds them back into the ozone destruction cycle. Isolation of the boundary layer air from the free troposphere by a strong temperature inversion was found to be critical for boundary layer ozone depletion to happen. The combination of strong surface inversions and presence of sunlight occurs only during polar spring.

1. Introduction

Reactive halogen species ($\text{RHS}=\text{X}, \text{X}_2, \text{XY}, \text{XO}, \text{OXO}, \text{HOX}, \text{XNO}_2, \text{XONO}_2$, where X, Y denotes a halogen atom) play a well recognised, central and largely understood role in the destruction of stratospheric ozone (e.g. Solomon 1990). Initially chlorine was investigated, however since the suggestion of the BrO-ClO cycle by McElroy et al. (1986) and Yung et al. (1980) and the subsequent detection of stratospheric BrO by

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Brune and Anderson (1986) and Solomon et al. (1989) it is clear that reactive bromine species also contribute considerably to the loss of stratospheric ozone.

While it has been argued that the abundance of inorganic halogen species should be small in the troposphere due to wet removal of the water soluble species (e.g. HBr) in recent years it became clear that reactive halogen species can play a significant role also in the troposphere. In the mid-1980s, sudden, complete boundary layer O₃ depletion at polar sunrise was observed by Oltmans and Komhyr (1986) at Point Barrow, Alaska and by Bottenheim et al. (1986) at Alert, Canada. During the depletion events ground-based O₃ mixing ratios decrease within hours from the mid-winter mean of 30 to 40 ppb to <1 ppb (parts per billion denote volume mixing ratio of 10⁻⁹=nmol/mol throughout this paper). The coincidence of the phenomenon with elevated particulate bromine at polar sunrise was subsequently noted by Barrie et al. (1988). Since then ground-based, balloon and aircraft observations have confirmed that O₃ depletion in the surface-based inversion layer over the Arctic Ocean is a widespread phenomenon (e.g. Hopper et al., 1998; Rasmussen et al., 1997; Solberg et al., 1996; Bottenheim et al., 2002).

As a common feature all observations of polar O₃ depletion events were made during the period mid-March to the end of May when sunlight is present at high latitudes and the Arctic Ocean is still frozen. This observation strongly suggests that photochemistry must play a key role in the responsible reaction schemes. On the other hand sunlight is also present during summer and fall, but no or only very weak ozone depletion is observed.

The vertical extend of O₃ depleted air masses typically range over the lowest 500 to 2000 m of the troposphere (Tuckermann et al., 1997; Martinez et al., 1999; Bottenheim et al., 2002). The downward mixing of ozone rich air from aloft is mostly prevented due to strong temperature inversions at the top of the boundary layer.

An important step towards an understanding of the relevant destruction processes was achieved with the detection of enhanced levels of BrO during depletion events in polar regions. In the Arctic BrO was observed by ground based active and passive

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DOAS (Differential Optical Absorption Spectroscopy, Platt, 1994) at Alert (Hausmann and Platt, 1994; Hönninger and Platt, 2002) and at Ny Ålesund (Tuckermann et al., 1997; Martinez et al., 1999), in Antarctica measurements were made by passive DOAS (Kreher et al., 1997; Frieß, 2001; Frieß et al., 2003). Mixing ratios of up to 30 ppt (parts per trillion denote volume mixing ratio of 10^{-12} =pmol/mol throughout this paper) BrO were detected simultaneous to complete ozone destructions. Those results strongly supported the theory of bromine catalysed ozone destruction in the polar troposphere.

In particular it could be shown that there is no detectable gradient in the BrO concentration inside the atmospheric boundary layer. Simultaneous measurements by two active long-path DOAS instruments at Ny Alesund, one light path running horizontally at about 50 m above sea level (Tuckermann et al., 1997), the other one from near sea level (20 m a.s.l.) to 474 m altitude (Martinez et al., 1999) found no systematic difference in BrO. In addition, recent studies employing MAX-DOAS (Multi Axis DOAS, Hönninger et al., 2004a) also allowed to study the vertical profile of BrO in the lowest kilometres of the atmosphere. It was shown that the enhanced BrO during ozone depletion is confined to the boundary layer (Hönninger and Platt, 2002; Hönninger et al., 2004b). Simultaneous active longpath DOAS and passive MAX-DOAS measurements allowed an even better determination of the vertical BrO profile. Excellent agreement with longpath DOAS BrO mixing ratios was found for data derived from MAX-DOAS column density measurements in case of a constant BrO mixing ratio over the vertical extent of the boundary layer (Hönninger et al., 2004b).

Despite several attempts ClO in the polar boundary layer was not detected unambiguously to date. Estimates based on upper limits gained by differential optical absorption spectroscopy (Tuckermann et al., 1997) and on calculations via Cl atom concentrations deduced from hydrocarbon destruction patterns (Jobson et al., 1994; Solberg et al., 1996; Ramacher et al., 1997, 1999), from determination by chemical amplification (Perner et al., 1999), or from measurements of BrCl (Foster et al., 2001; Spicer et al., 2002) suggest ClO mixing ratios during depletion events of the order of a few ppt.

During springtime large parts of the Arctic basin are subject to ozone depletion.

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Satellite observations of tropospheric BrO column densities (Richter et al., 1998; Wagner and Platt, 1998; Wagner et al., 2001; Hollwedel et al., 2004) provided first information about the extension of the regions where ozone depletion is in progress. During spring areas exceeding 10^7 km^2 (about 2% of the earth's surface) might be affected at any given time.

There are strong indications that similar surface O_3 destruction also occurs at polar sunrise in Antarctica. Ozone depletion events during Austral spring were reported from Syowa, Neumayer Station and Arrival Heights (Murayama et al., 1992; Wessel et al., 1998; Kreher et al., 1997). The tropospheric BrO observations via satellite measurements support the ground based measurements at Antarctica. It is interesting to note, that the satellite measurements indicate that high BrO levels are restricted to coastal areas and the sea ice belt around Antarctica (e.g. Wagner et al., 2001).

To date this process appears to have only few parallels outside polar regions (Platt and Hönninger, 2003; Sander et al., 2003). However, even higher BrO mixing ratios (up to 172 ppt) were detected by optical absorption spectroscopy (DOAS) in the Dead Sea basin during summer (Hebestreit et al., 1999; Matveev et al., 2001). Recently significant BrO abundances were also reported from Great Salt Lake, Utah, USA (Stutz et al., 2002) and from Salar de Uyuni, Central Altiplano, Bolivia (Hönninger et al., 2004c). In addition, evidence is accumulating that BrO (at levels around 1–2 ppt) is also occurring in the free troposphere (in polar regions as well as at mid-latitudes) (McElroy et al., 1999; Ferlemann et al., 1998; Frieß et al., 1999; Fitzenberger et al., 2000; Pundt et al., 2000; van Roozendael et al., 2002).

2. The mechanism of ozone depletion

With the above mentioned observations it is meanwhile state of knowledge that reactive halogens (e.g. Br, Cl) are responsible for the ozone destruction.



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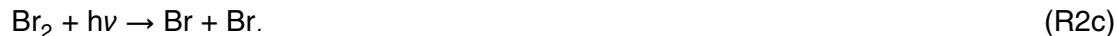
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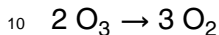
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The conversion of BrO (or ClO) back to reactive Br (r-Br) or r-Cl allows one halogen molecule to destroy more than one O₃ molecule. These conversion reactions are slower than (R1) and therefore they include the rate limiting step in the destruction cycle:

5 1.



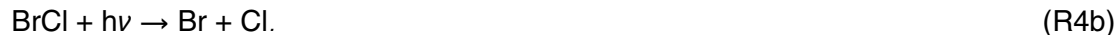
Net effect of (R1)+(R2a)–(R2c):



2.



3.



20 (R2a)+(R2b), (R3a) and (R4a) are the rate limiting steps for the individual reaction channels. Under the assumption of 20 ppt BrO, 2 ppt ClO and 1 ppt HO₂, (R2) is responsible for 45% of the ozone destruction, (R3) for 40% and the cross reaction between BrO and ClO accounts for 15% of the O₃ destruction.

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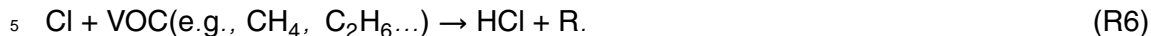
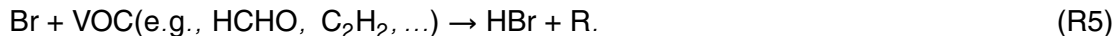
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To assess the relative O₃ destruction potential of Br and Cl, the probabilities for halogen reaction with VOCs (volatile organic compounds) (R6) has to be taken into account.



The branching ratio between the reaction channels leading to a back conversion into reactive halogen atoms and those reactions channels, which promote reactive halogens out of the O₃ destruction cycle via (R5) or (R6) are different for bromine and chlorine atoms. Under typical Arctic conditions (40 ppb O₃ and VOC concentration from Ramacher et al. (1999), see Table 6) 98% of Br, but only 50% of Cl reacts with O₃.

The BrO lifetime is controlled by its photolysis and is approximately 100 s. The cross reaction BrO + ClO determines the ClO lifetime also to 100 s (20 ppt BrO assumed). Together with the above mentioned branching ratios this leads to effective lifetimes versus conversion to HX (via R5 or R6) of 5000 s and 200 s for BrO_x and ClO_x, respectively. This ratio explains the dominant role of bromine chemistry in tropospheric ozone destruction compared to those of ClO and HOCl.

The calculated BrO_x lifetime is by far too short to destroy all ozone molecules within the boundary layer. With the above listed reactions only a few ppt of ozone would be destroyed before bromine would accumulate as HBr. For a complete ozone depletion a constant level of 20 ppt BrO for at least a day (or roughly 100 000 s) is required. Therefore an efficient and fast halogen recycling from unreactive HX to r-Br (reactive bromine) and r-Cl (reactive chlorine) is necessary to obtain a complete ozone loss. It was demonstrated by several laboratory and modelling studies, that heterogeneous reactions on aerosol surfaces might stand for such necessary halogen recycling (Fan and Jacob, 1992; Abbatt, 1994, 1995; Mozurkewich, 1995; Tang and McConnell, 1996; Vogt et al., 1996; Kirchner et al., 1997; Abbatt and Nowak, 1997; Sander et al., 1997; Fickert et al., 1999).

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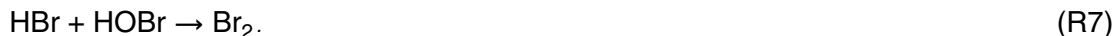
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Following the results from those studies, HBr, HCl and HOBr, HOCl are scavenged by aerosol particles and liquid phase reactions within the aerosol phase can lead to the production of Br₂ or BrCl.



Both products are rejected to the gas phase and can be converted back to r-Br or r-Cl by photolysis. Together with those autocatalytic halogen recycling processes, once 20 ppt r-Br are in the gas phase, complete ozone depletion is possible in a day.

3. The source of reactive halogen species (RHS)

10 Although the mechanism leading to O₃ depletion seems to be well understood, it is still unclear how reactive halogen species (RHS) originally enter the gas phase. As discussed previously (Barrie et al., 1988; Fan and Jacob, 1992; Tang and McConnell, 1996; Tuckermann et al., 1997) two possible sources of RHS during Arctic spring are:

1. liberation from sea salt either in the aerosol or on the Arctic ocean ice surface, or
- 15 2. degradation of organohalogen compounds of anthropogenic or natural origin.

Due to the relatively long photolysis lifetime of the most abundant gaseous organohalogens (e.g. CH₃Br, CHBr₃, CHBr₂Cl) under polar springtime conditions, the latter source is unlikely. However, strong evidence has emerged, which shows that atmospheric reactions involving oxidants lead to auto-catalytic liberation of r-Br from sea salt reservoirs (sea salt containing by weight 55.7% Cl, 0.19% Br, and 0.00002% I), that can be released to the atmosphere as gaseous reactive halogen species (e.g. Cl₂, Br₂ or BrCl). Proposed reaction sequences involve NO_y species (Finlayson-Pitts et al., 1990) HOBr (Fan and Jacob, 1992; McConnell et al., 1992), HOCl, or other oxidants such as

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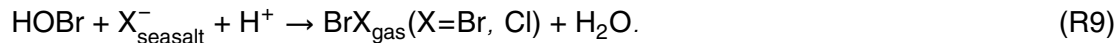
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H₂O₂ (Wessel et al., 1997). However, recent measurements of NO_x in the Arctic seem to rule out nitrogen species (e.g. N₂O₅) as the oxidant. In principle those processes should work at both sea salt reservoirs: airborne sea salt aerosol particles and the surface of the sea ice. The differences and relative importance of both reservoirs will be discussed in the next section.

Several modelling studies (Fan and Jacob, 1992; Sander and Crutzen, 1996; Vogt et al., 1996), as well as laboratory studies (Abbatt, 1994; Fickert et al., 1999; Kirchner et al., 1997) indicate that autocatalytic processes via HOBr are responsible for halogen release:



Once Br₂ or BrCl is in the gas phase it can be photolysed rapidly to release halogen atoms, which subsequently will start ozone destruction (R1). This autocatalytic bromine release mechanism resulting in an exponential increase of gas phase bromine is referred to as “Bromine Explosion” (Platt and Lehrer, 1997 as quoted by Wennberg, 1999).

The role of HOBr within the bromine explosion mechanisms is twofold: 1) HOBr drives the primary halogen activation out of the sea salt reservoir and 2) for the autocatalytical recycling of HX on the surface of aerosol particles. One Br_x is recycled via heterogeneous reactions on aerosol surfaces roughly 30 times before it can promote a new Br_x via the primary activation process to the atmosphere. In other words about 3% of total HOBr is available for the primary Br_x production.

HOBr is mainly produced by reactions of BrO with HO₂, CH₃O₂ and R'O₂ (R' = org. group, except CH₃). The production of HOBr therefore strongly depends on the availability of peroxy radicals RO₂ (R=H, CH₃, R'). The HO₂ production rate must therefore exceed the production of HBr. Assuming that the alkyl rest produced by reaction R5 leads to at least one HO₂ molecule, all HBr can be recycled back to r-Br.

Any HO₂, which is in excess, is available to promote new bromine into the destruction cycle by primary processes. The source strength of HO₂ (CH₃O₂–R'O₂) seems to be a critical point for halogen activation.

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The major production pathways for HO₂ are initiated by ozone and formaldehyde photolysis.



An estimation of the HO₂ production rate via this mechanism ($J_{\text{R10}} = 4.7 \times 10^{-7} \text{ s}^{-1}$, branching ratio for OH production from O¹D+H₂O, $v = 0.8 \times 10^{-2}$; $[\text{H}_2\text{O}] = 2.2 \times 10^{16}$; $[\text{O}_3] = 10^{12} \text{ cm}^{-3}$) provides 40 ppt HO₂ per day.

3.1. The primary halogen source: Sea salt aerosol or sea ice

10 While it is very likely that bromine liberation from sea salt is the source of the observed BrO, no satisfying answer is presently available, whether the sea salt contained in the aerosol or on the sea ice surface (or snow pack) is the source of reactive bromine species during polar tropospheric ozone depletion.

15 Sander and Crutzen (1996) pointed out that liberation processes from sea salt aerosol might lead to ozone depletion in the remote marine atmosphere. However, the sea salt concentrations in polar regions are lower compared to those at open sea conditions. Aerosol measurements at Ny Ålesund/Spitsbergen (Langendörfer et al., 1999; Lehrer et al., 1997) provide typical concentration levels between 0.1 and 1 μg m⁻³ (see Table 1). The maximum concentrations were observed in winter and early spring together with maximum average wind speed. With an estimated atmospheric lifetime of
20 sea salt aerosol particles of 2 days and under the assumption that the liberation of reactive halogen molecules by the above mentioned processes is fast compared to the residence time of the aerosol, the observed sea salt concentrations can account for up to few ppt of photolysable bromine. To explain the observed levels of BrO (up to 30 ppt) or total bromine (up to 80 ppt) halogen release out of sea salt aerosol has to occur over
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a period of more than one week. This is not in accordance with estimates for the actual time period of an event of complete ozone depletion, which is in the range of 2–3 days (e.g. Sander et al., 1997).

5 Although maximum sea-salt aerosol concentrations can be several times the average levels the available amount of aerosol bromine is at least one order of magnitude too low to explain the observed BrO levels. Therefore it is unlikely that sea salt aerosol is the primary source of reactive bromine in the polar troposphere and sea-salt deposits on ice have to be considered in addition. Thus the “well-mixed atmosphere” picture used in earlier modelling studies (Sander and Crutzen, 1996; Vogt et al., 1996) cannot
10 be correct, since these studies base on the assumption that all primary halogen species are already airborne.

Tang and McConnell (1996) suggested that halogen liberation may be possible from halogen deposits on the snow pack. The mobilisation out of the snowpack can help to reactivate bromine, which was scavenged by snow flakes and then deposited. However
15 there is no reason, why the snow pack should serve as primary sea salt reservoir.

On the other hand the fresh sea ice surface is known to act as a huge reservoir of halogens (Perovich and Richter-Menge, 1994). The freezing process of sea water leads to a thin liquid film on top of the sea ice surface. This brine solution is highly enriched in sea salt and reaches typical salinity values up to 100 psu (3 times the salinity of sea water; 1 psu=10 g sea salt per l sea water). Also the growing of crystals,
20 which were enriched in sea salt was observed. Wolff and Martin (1998) suggested that frost flowers may serve as source for sea salt aerosol at Antarctic coastal areas.

Under typical Arctic conditions the vertical atmospheric column over the lowest 1000 m contains 10^{-3} cm^2 of reactive aerosol surface per cm^2 of ground surface (Staebler et al., 1999). In comparison the sea ice surface provides 1000 times the reactive surface compared to the sea salt aerosol. Taking into account that the sea ice surface is not flat, but may be covered by e.g. frost flowers it likely provides an even greater reaction surface for halogen liberation.

If all the bromine which is contained inside a 1 mm thick brine layer of 100 psu was

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released to the gas phase as reactive Br this would correspond to gas phase mixing ratios of up to 55 ppb Br in the lowest 1000 m. This mixing ratio is 2 orders of magnitude higher than the observed levels of reactive bromine during ozone depletion events. It is clear, that the sea ice surface provides a nearly inexhaustible source. On the other hand – in the case of a surface source – transport limitations between the phase boundary and the atmosphere have to be taken into account.

Several laboratory studies suggested that the HOX (X = Br, Cl) catalysed halogen mobilisation out of sea salt reservoirs requires a low pH of the reservoir. Fickert et al. (1999) pointed out, that below pH=6.5 sea salt solutions are very efficient bromine sources. Therefore no liberation from the ocean surface (pH=8.4) is to be expected. Aerosol measurements in the Arctic provide very acidic conditions, indicated by high sulfate concentration levels during Arctic Haze season (January–April). In Antarctica tropospheric ozone depletion and elevated levels of BrO are observed at sulfate concentrations which are at least one order of magnitude lower. However, although it is believed to have natural causes, Arctic haze sulphate aerosols and gaseous pollutants advected from Europe, Russia and to a lesser extent, North America may also contribute.

There is only little information available on the pH of the fresh sea ice surface. Adams et al. (2002) performed laboratory investigations into halogen activation out of frozen sea salt solutions. Their results, that the activation depends on cold temperatures rather than on acidity might be a simple solution why bromine explosion is also observed under non-acidic conditions at the Antarctic sea ice belt.

In summary, presently there exists no coherent theory that explains all observed features of the “Polar tropospheric ozone hole”, in particular there are the following open questions:

Does the bromine come from sea-salt deposits or aerosol?

- What is the role of chlorine?
- Why does it occur only in polar regions?

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- Why is halogen activation related to ozone depletion only observed in springtime, i.e. after sunrise, but not during summer and fall?
- What causes the episodic nature of the events?

To clarify these questions, we will discuss here available data from field measurements and present 1D model calculations of the key processes. Based on those results we present a consistent theory of the processes that gives satisfactory answers to the above questions.

Figure 1 shows the general picture of bromine chemistry including gas phase and heterogeneous reactions, but neglecting chlorine chemistry for the sake of simplicity.

4. Model description

The presented model was developed with the aim to obtain a quantitative understanding of the concurring liberation processes from sea salt reservoirs at the ground and in the aerosol and to help answering the question whether sea salt aerosol or the sea ice surface is responsible for bromine release in the polar springtime troposphere. This was attempted by including halogen activation processes from sea ice and from sea salt aerosol into the model and by comparing the respective time scales of both liberation mechanisms. In the case of the sea ice surface the transport of the relevant species between the upper part of the boundary layer and the phase boundary to the sea ice has to be implemented into the model.

The model was written in FACSIMILE developed by the British Atomic Energy Agency (FACSIMILE, 1992), which was previously also used by Vogt et al. (1996) and Sander and Crutzen (1996) for their modelling studies.

4.1. Vertical transport in the model

The transport limitations between sea ice and lower troposphere are realized by defining a vertical model structure and dividing the virtual boundary layer into 8 stacked ver-

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tical boxes (see Fig. 2). The major assumption bases on a boundary layer of 1000 m height, which is stably stratified and topped by an inversion layer. The height of the boxes is growing from the surface in a logarithmic scale, with the lowest box 0.09 μm high and the top box 900 m high. The inversion situation above the boundary layer was represented in the model by not allowing exchange between the top box and the layer above (i.e. free troposphere) in the base run of the model.

Within each individual box all included species (compare Table 3) are assumed to be well mixed and the exchange between individual boxes was characterized by respecting turbulent mixing $K(z)$ as well as molecular diffusion D :

$$J_{\downarrow,\uparrow} = -(K(z) + D) \frac{\Delta[X]}{\Delta z}, \quad (2)$$

where $J_{\downarrow,\uparrow}$ is the upward or downward directed flux between the boxes, $\Delta[X]=[X_{i+1}]-[X_i]$ (i = number of box) the concentration difference between neighbouring boxes and Δz the vertical distance between the centres of two neighbouring boxes. In case of neutral stratification the coefficient of turbulent diffusion $K(z)$ is known to be a linear function of height z .

The concentration change for each box i per time step is calculated as the sum of the volume source strength P_i and the volume sink D_i , together with upward and downward directed flux J_{\uparrow} and J_{\downarrow} divided by the height l_i of box i .

$$\frac{d[X]_i}{dt} = P_i - D_i + \frac{J_{\downarrow}}{l_i} + \frac{J_{\uparrow}}{l_i}. \quad (3)$$

P_i and D_i denote volume sources and sinks by chemical (gas phase and heterogeneous) reactions.

4.2. Representation of the aerosol in the model

Aerosol particles can serve as substrate for heterogeneous reactions. The model includes the heterogeneous reactions of $\text{HOBr} + \text{Br}^-$, $\text{HOBr} + \text{Cl}^-$ and $\text{HOCl} + \text{Br}^-$ on

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aerosol surfaces. It is assumed that the recycling surface is provided only by sulfate particles, which contributes more than 95% of the total aerosol surface under typical Arctic springtime conditions (Staebler et al., 1999). The typical parameters of the sulfate aerosol were normalized according to the results of Staebler et al. (1999), where $a=0.45\text{ }\mu\text{m}$ denotes the aerosol radius, $A=100\text{ }\mu\text{m cm}^{-3}$ the aerosol surface and $V=10\text{ }\mu\text{m}^3\text{ cm}^{-3}$ the aerosol volume.

According to Hanson et al. (1994) the uptake-coefficient γ is calculated as:

$$\frac{1}{\gamma_{\text{spherical}}} = \frac{1}{\alpha} + \left[\frac{4RTH\sqrt{D_{\text{liq}}k'_{\text{liq}}}}{v_{\text{therm}}} \left(\coth\left(\frac{a}{l}\right) - \frac{l}{a} \right) \right]^{-1}, \quad (4)$$

where R , T denote the universal gas constant and the absolute temperature, respectively. The Henry-coefficients H , liquid reaction rates k_{liq} , and diffusion coefficient D_{liq} were taken from the work of Abbatt and co-workers (see Table 2). According to those studies an accommodation coefficient $\alpha=1$ was assumed. Halogen uptake was corrected for the curved aerosol surface by the last term in the brackets of Eq. (3) with the

help of the diffusive-reaction length $l = \sqrt{\frac{D_{\text{liq}}}{k'_{\text{liq}}}}$.

The production rate of the di-halogen molecules Y_{gas} (Br_2 or BrCl) is calculated according to Schwartz (1986), with X_{gas} being the limiting reaction partner (HOX or HX) in the liquid phase.

$$\frac{d[Y_{\text{gas}}]}{dt} = -\frac{d[X_{\text{gas}}]}{dt} = \left(\frac{a}{D_g} + \frac{4}{v_{\text{therm}}\gamma} \right)^{-1} A_{\text{surface}} [X_{\text{gas}}] \quad (5)$$

An HOBr uptake coefficient $\gamma=0.12$ is calculated from Eq. (3) at a gas phase mixing ratio of 10 ppt HBr . Together with 10 ppt HOBr this corresponds to a HOBr loss rate (or Br_2 production rate) of $1.8 \times 10^5\text{ molecules cm}^{-3}\text{ s}^{-1}$.

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In the base run of the model sea salt aerosol as a primary halogen source was not considered. A variant of the model to test for the potential of the aerosol source is described in Sect. 5.3.

4.3. Representation of the sea ice surface in the model

5 The sea ice surface is coupled to the model by allowing exchange between a sea salt reservoir and the lowest box of the model. Included are all reactions between HOBr and HOCl and sea salt. The halogen content in the sea ice layer is assumed to be an inexhaustible source. The uptake coefficient of HOX onto the sea ice surface was chosen $\gamma=0.06$ after Sander and Crutzen (1996).

10 The most important products of the heterogeneous HOX reactions at the sea ice surface are Br₂ and BrCl. Due to the small abundance of HOCl, the production of Cl₂ is negligible. Therefore the branching ratio between Br₂ and BrCl production plays a key role. The branching ratio of Br₂ to BrCl activation was chosen 40 to 60%, respectively. This ratio is in accordance with the results of Kirchner et al. (1997) and provides a very
15 conservative assumption in regard to the studies of Fickert et al. (1999) and Adams et al. (1999). The latter found that under cold temperature conditions ($<-15^{\circ}\text{C}$) Br₂ is almost exclusively produced by the primary production processes at the sea ice surface.

4.4. Gas phase chemistry

20 The gas phase species included in the model are listed in Table 3. Reaction rates were calculated assuming a temperature of 258 K. Most of the reaction constants were calculated using the data published in (Atkinson et al., 1997). Reaction constants which were not documented there are listed together with the literature citation in Table 4.

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4.5. Photochemistry

All presented runs of the model were calculated by assuming a fixed sun zenith angle (SZA=80°). The photolysis frequencies were calculated using the model of R \ddot{o} th (R \ddot{o} th et al., 1996) and are listed in Table 5. A comparison of results with a model run under the simulation of diurnal and monthly SZA variations provided no substantial difference in time scale of ozone depletion and absolute concentration levels of relevant species.

4.6. Initial mixing ratios

The initial mixing ratios used for the simulation are listed in Table 5. The hydrocarbon mixing ratios are adapted to the results of Ramacher et al. (1997). Initial bromine and chlorine mixing ratios are present in their molecular form, which guarantees via photolysis a rapid distribution into all gaseous halogen species included in the model. The (unrealistic) assumption of equal amounts of bromine and chlorine in the model was made to compare the respective role of each halogen.

5. Results and discussion

The concentration records for ozone and the most important bromine species are demonstrated for the model box representing the upper part of the boundary layer (100–1000 m) as shown in Fig. 3. The onset of a fast ozone depletion occurs around day 35 of the simulation and within 5 days the ozone concentration drops to immeasurable low values. Other simulations with different initial halogen concentrations demonstrate that higher or lower initial halogen concentrations results in a shorter or longer initial period, respectively, but the time scale in which most of the ozone is destroyed remains almost the same.

The maximum ozone destruction rate of 7.6 ppb per day is observed during the end of the depletion process. 90% of initial 40 ppb O₃ are destroyed within 5 days. This

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value lies in the range of previous assumptions but at the upper end of previous suggestions (compare Hausmann and Platt, 1994).

During the initial phase HOBr is the dominating bromine species. Shortly after the onset of rapid ozone destruction BrO takes over the role as major bromine species.

5 With decreasing ozone BrO production slows down and finally at $O_3 < 2$ ppb, the probability of BrO production is negligible compared to the HBr (R5) channel. The maximum BrO levels of 20 ppt are comparable to field measurements at Alert (Hausmann and Platt 1994, Hönninger and Platt, 2002) and at Spitsbergen (Tuckermann et al., 1997; Martinez et al., 1999).

10 At the end of the depletion process all Br is accumulated in form of HBr. This was already suggested by Langendörfer et al. (1999) and supported by their aerosol measurements, where high levels of filterable bromide, possibly represented by additional HBr, were found on aerosol filters.

This model run also provides information on the vertical gradients of the key species (see Fig. 4). The ozone concentration is distributed homogeneously inside the whole column throughout the depletion process. This is consistent with findings from ozone soundings, which suggest that the ozone concentration is almost constant within the boundary layer (e.g. Bottenheim et al., 2002).

20 The simulated BrO profile (Fig. 4) suggests a small concentration gradient between the lowest meter and all layers above, which was in fact seen by the several field studies as discussed in the introduction.

According to our model appreciable amounts of Br_2 should only be present in the lowest meter above the sea ice (Fig. 4, lowest panel). While ascending from the phase boundary up to the free atmosphere most of the Br_2 is photolysed within the lowest centimetres. The first measurements of Br_2 and BrCl during polar sunrise 2000 by Foster et al. (2001) actually confirmed up to 25 ppt Br_2 and 35 ppt BrCl, respectively at 125 cm above the snow pack. As the solar zenith angle during these measurements was close to 90° , photolysis is significantly slower resulting in higher concentrations of photolabile species. On the other hand almost all HOBr is consumed by reactions

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on the sea ice surface. Therefore HOBr mixing ratios in the order of several ppt are observed only in the upper box (Fig. 4, second to lowest panel).

5.1. The role of chlorine

5 An important question in the chemical processes of ozone destruction is the role of chlorine atom chemistry. Unlike the stratosphere chlorine atom chemistry plays a minor role in direct destruction of boundary layer ozone. However, Rudolph et al. (1999) suggested that chlorine atom chemistry might be important for HO₂ production. Presently no method has been able to directly detect chlorine atoms. The best estimates of chlorine atom concentrations are deduced from the destruction patterns of specific hydrocarbons (hydrocarbon clock).
10 Rudolph et al. (1999) and Ramacher et al. (1999) found time integrated chlorine atom concentrations of $10^{10} \text{ s cm}^{-3}$. With an assumed time period for ozone depletion process of 1 day this corresponds to a chlorine atom concentration of $1.2 \times 10^5 \text{ cm}^{-3}$ ($2.3 \times 10^4 \text{ cm}^{-3}$ for 5 days).

The model results for chlorine species for the base run are shown in Fig. 5.
15 The model provides maximum chlorine atom concentrations of $1.2 \times 10^3 \text{ cm}^{-3}$ and integrated chlorine atom concentration over the whole depletion process of $1.1 \times 10^9 \text{ s cm}^{-3}$. The chlorine atom concentrations in the model are at least one order of magnitude lower than field observations suggest. The role of chlorine chemistry is underestimated within this model. Therefore the loss of alkanes due to chlorine atoms chemistry is only 1/3 of which is observed under Arctic conditions (Ramacher et al., 1999).
20

One possible reason might be the unrealistic low initial chlorine concentration or the decomposition of organo-chlorine compounds which are not implemented in the model. The consequences might be that peroxy radical formation due to chlorine atom reactions could be more important in reality, as suggested by Rudolph et al. (1999).
25 However, the model results support the results of Fickert et al. (1999), which concluded, that the observed levels of chlorine atoms in the marine boundary layer are very unlikely due to halogen activation out of sea salt.

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However it is noteworthy that additional HO₂ production by chlorine atom chemistry is not necessary in order to explain the observed BrO levels and degree of O₃ depletion.

5.2. Role of boundary layer inversions

Additional model runs allowing turbulent diffusion from the free troposphere into the boundary layer were performed and are summarized in Fig. 6. It is clear that significant entrainment of ozone-rich air from the free troposphere prevents complete ozone depletion in the boundary layer. While turbulent diffusion coefficients up to $2 \times 10^3 \text{ cm}^2 \text{ s}^{-1}$ only slow down ozone loss in the boundary layer, for K exceeding $5 \times 10^3 \text{ cm}^2 \text{ s}^{-1}$ no complete ozone depletion in the boundary layer appears.

Therefore we conclude that complete ozone depletion in the boundary layer can only be observed if dilution of the reactive bromine and down-mixing of ozone rich air from aloft are prevented by a strong inversion at top of the boundary layer. The standard simulation of the model does not allow any transport across the top of the surface based inversion layer.

5.3. Aerosol as additional halogen source

In order to study the role of aerosol in an additional model run it was assumed that sea salt aerosol production and the subsequent deposition of those particles leads to a constant bromine content in the aerosol equalling the amount contained in $1 \mu\text{g m}^{-3}$ sea salt. The production rates were identical inside each box. To simplify the calculations the sea salt aerosol halogen content was put into the model in its inactive form either as HBr or HCl, respectively:

$$\frac{d[\text{HX}]}{dt} = + \frac{1}{\tau_{\text{aerosol}}} [\text{HX}]_{\text{seasalt}} - \frac{1}{\tau_{\text{aerosol}}} [\text{HX}]_{\text{aq}} \quad (6)$$

The first term on the right side of Eq. (5) describes the formation of sea salt aerosol, the second term, the deposition of HX, which is scavenged in the aerosol. $[\text{HX}]_{\text{aq}}$ was

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calculated over the phase ratio between liquid and gaseous fraction of HX. The aerosol lifetime τ_{aerosol} was assumed to be 2 days.

These assumptions might overestimate the influence of the halogen source strength due to sea salt aerosol. This is due to the simplification that all fresh halogens which are transported via the sea salt aerosol into the upper layers of the boundary layer are transferred into the autocatalytic recycling mechanism

Therefore the results of this modification shown in Fig. 7 indicate the maximum influence of the sea salt aerosol as source.

Under the same initial conditions as used in the standard simulation, complete ozone depletion occurs after 25 days. But no differences are observed in the amount of released bromine and in the time scale of the last part of the depletion process.

5.4. Comparison of different model runs

To investigate in the importance of each individual step of the bromine explosion cycle the base run (variation A – sea ice surface sole halogen source) was compared to the other model runs (Fig. 8):

- variation B: aerosol plus surface source but halogen recycling on aerosol surface excluded;
- variation C: only sea salt aerosol as source for RHS implemented;
- variation D: sea salt aerosol plus sea ice surface as potential halogen source.

The fastest ozone depletion was obtained under the assumption that both – the sea ice surface and sea salt aerosol particles – serve as source for reactive halogen species (D). However, the maximum rate of ozone destruction was not slower without the consideration of the aerosol source (A). The amount of total gas phase Br within the boundary layer at the end of the depletion process is almost equal for both assumptions (A and D). On the other hand halogen activation out of sea salt aerosol particles (C) alone is by far too slow to account for a fast ozone depletion.

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Without halogen recycling at the surface of aerosol particles (B) no exponential growth of the bromine species can be obtained.

6. Conclusions

The presented model compared the role of the two concurring halogen sources: activation out of sea salt aerosol and out of the sea ice surface. The model calculations together with information about typical sea salt aerosol concentrations in the Arctic boundary layer demonstrated that sea salt aerosol is a minor source compared to the potential of the sea ice surface source strength.

Halogen activation from the (brine layer on the) sea ice surface as single source leads to an exponential growth of reactive halogen species in the boundary layer. 90% of initial 40 ppb ozone are destroyed within the last 5 days of the depletion process. The duration of the initial depletion phase depends on the amount of reactive bromine available at the beginning of the simulation. A Br or Cl threshold concentration to trigger a bromine explosion is not necessary. For 0.6 ppt of initial Br_x and Cl_x the initial phase lasts 35 days.

However, two critical points for the success of a bromine explosion could be scrutinised:

1. The significance of pH<6.5 for the primary sea salt reservoir is not completely proven. There are indications that the sea salt aerosol might be sufficiently acidified. The conditions of the sea ice surface are presently not examined. Here we suggest field experiments to investigate in the ionic composition of young and aged sea ice surfaces as well as frost flowers.
2. The availability of peroxy radicals, namely HO₂, as precursors for HOBr is still unclear. We suggested that the reactions of halogens with VOCs might lead to the production of at least one HO₂ molecule per X + VOC reaction. The amount of HO₂ which is required to produce new Br_x over primary source processes can

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be provided via the photolysis of ozone and formaldehyde as discussed above. The production channel of HO₂ via ozone photolysis accounts only for 25% of the total production rate.

Strong gradients in the lowest meter above the surface are found for HOBr, Br₂ and BrCl, with the first species not at all and the others exclusively observed in the lowest meter of the atmosphere.

It is demonstrated that halogen recycling at aerosol surfaces is necessary to keep enough bromine in the active reservoir. A bromine atom is recycled about 30 times before it can activate a new Br atom via the primary processes.

Prerequisites for a polar bromine explosion are:

- Availability of sea salt surface (brine, dry salt, or possibly frost flowers) on sea ice.
- Strong temperature inversion at top of the boundary layer.
- Sun light.

The seasonal changes of the prerequisites for bromine explosions and ozone depletions are summarised in Fig. 9. In polar regions all three prerequisites are only fulfilled after polar sunrise during polar spring (see Table 7). Ozone depletion events in the polar boundary layer are not seen in winter (i.e. the polar night), summer, and fall. The sea ice surface not only decreases strongly during polar summer, but also the amount of sea salt on the ice surface decreases as melt water efficiently transports surface salt through cracks back into the ocean. Strong temperature inversions are also only typical for polar spring as continuous solar radiation enhances convection during the summer months. Polar fall is typically very short and - although new sea ice starts forming during this time - areas of open ocean prevent strong temperature inversions.

There are indications that weak events, not detectable by satellite, and not causing noticeable ozone depletion, may sometimes also occur in summer and fall, studies of this phenomenon are in progress. However, as discussed above, conditions favourable for bromine explosions appear in certain areas outside polar regions, where large salt

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deposits provide surfaces from which reactive bromine can be released. The role of temperature inversions (and topography) in these cases remains to be investigated.

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Table 1. List of input parameters.

Typ. Levels (total weight) of sea salt aerosol	0.4–4 μgm^{-3}
Br – fraction thereof (0.19%)	0.8–8 ngm^{-3}
Equivalent gas phase mixing ratio (at -15°C)	0.2–2 ppt
Observed levels:	up to 30 ppt BrO up to 80 ppt total Br

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Table 2. Parameters of liquid phase reactions in the aerosol phase used in the model after Abbatt and co-workers (Abbatt, 1994, 1995; Abbatt and Nowak, 1997; Waschewsky and Abbatt, 1999).

	HBr	HOBr	HCl	HOCl
H^* (M atm ⁻¹)	3×10^8	1.7×10^4	3×10^6	1.7×10^5
D_{liq} (cm ² s ⁻¹)	5×10^{-6}	5×10^{-6}	5×10^{-6}	5×10^{-6}
k^{II} (M ⁻¹ s ⁻¹)	5.0×10^4 (HBr/HOBr)		1.0×10^5 (HCl/HOBr)	
	2.0×10^6 (HBr/HOCl)		Not included (HCl/HOCl)	

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Table 3. List of chemical species in the model.

Family	species
O _x	O ₃ O ₂
HO _x	H ₂ O OH HO ₂ H ₂ O ₂
NO _x	N ₂ NO NO ₂ NO ₃ HNO ₃ HONO HNO ₄ PAN
VOC	CO CO ₂ CH ₄ C ₂ H ₆ C ₂ H ₅ C ₂ H ₄ C ₂ H ₂ C ₃ H ₈ HCHO CH ₃ CHO CH ₃ OO CH ₃ OOH CH ₃ OH CH ₃ CH ₂ OO CH ₃ CH ₂ OOH CH ₃ CO ₃ CH ₃ CH ₂ O
Br _x	Br ₂ Br BrO HBr HOBr BrNO ₂ BrONO ₂
Cl _x	Cl ₂ Cl ClO OCIO ClOO HCl HOCl Cl ₂ O ₂ BrCl ClONO ₂

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Table 4. Constants for reactions used in the model, which are not taken from Atkinson et al. (^a Mocalce, Sander et al., 1997; ^b Borken, 1996; ^c Barnes et al., 1993; ^d DeMoore et al., 1997; ^e Sander and Crutzen, 1996; ^f Aranda et al., 1997).

$\text{C}_2\text{H}_4 + \text{O}_3$	$\rightarrow \text{HCHO} + \text{CO}$	4.33×10^{-19}	^a
$\text{C}_2\text{H}_5\text{O} + \text{O}_2$	$\rightarrow \text{CH}_3\text{CHO} + \text{HO}_2$	7.44×10^{-15}	^a
$\text{C}_2\text{H}_5\text{O} + \text{O}_2$	$\rightarrow \text{CH}_3\text{O}_2 + \text{HCHO}$	7.51×10^{-17}	^a
$\text{C}_2\text{H}_5\text{OOH} + \text{OH}$	$\rightarrow \text{C}_2\text{H}_5\text{O}_2 + \text{H}_2\text{O}$	8.21×10^{-12}	^a
$\text{C}_2\text{H}_5\text{OOH} + \text{Cl}$	$\rightarrow \text{C}_2\text{H}_5\text{O}_2 + \text{HCl}$	5.70×10^{-11}	^a
$\text{C}_2\text{H}_5\text{OOH} + \text{Br}$	$\rightarrow \text{C}_2\text{H}_5\text{O}_2 + \text{HBr}$	5.19×10^{-15}	^a
$\text{BrO} + \text{CH}_3\text{O}_2$	$\rightarrow \text{Br} + \text{HCHO} + \text{HO}_2$	1.60×10^{-12}	^f
$\text{BrO} + \text{CH}_3\text{O}_2$	$\rightarrow \text{HOBr} + \text{HCHO}$	4.10×10^{-12}	^f
$\text{Br} + \text{C}_2\text{H}_2$	$\rightarrow 2 \text{CO} + 2 \text{HO}_2 + \text{Br}$	4.20×10^{-14}	^b
$\text{Br} + \text{C}_2\text{H}_2$	$\rightarrow 2 \text{CO} + \text{HO}_2 + \text{HBr}$	8.92×10^{-14}	^b
$\text{Br} + \text{C}_2\text{H}_4$	$\rightarrow 2 \text{CO} + 2 \text{HO}_2 + \text{Br}$	2.52×10^{-13}	^c
$\text{Br} + \text{C}_2\text{H}_4$	$\rightarrow 2 \text{CO} + \text{HO}_2 + \text{HBr}$	5.34×10^{-13}	^c
$\text{Cl} + \text{C}_2\text{H}_4$	$\rightarrow 2 \text{CO} + 2 \text{HO}_2 + \text{Cl}$	2.00×10^{-11}	^b
$\text{Cl} + \text{C}_2\text{H}_4$	$\rightarrow 2 \text{CO} + \text{HO}_2 + \text{HCl}$	4.24×10^{-11}	^b
$\text{OCIO} + \text{NO}$	$\rightarrow \text{NO}_2 + \text{ClO}$	2.44×10^{-13}	^d
$\text{Br}_2 + \text{Cl}$	$\rightarrow \text{BrCl} + \text{Br}$	1.20×10^{-10}	^e
$\text{BrCl} + \text{Br}$	$\rightarrow \text{Br}_2 + \text{Cl}$	3.30×10^{-15}	^e
$\text{Br} + \text{Cl}_2$	$\rightarrow \text{BrCl} + \text{Cl}$	1.10×10^{-15}	^e
$\text{BrCl} + \text{Cl}$	$\rightarrow \text{Br} + \text{Cl}_2$	1.50×10^{-11}	^e

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Table 5. Photolysis reactions in the model and photolysis rates calculated for SZA = 80° after the model of Roeth (1996).

	J (s ⁻¹)		J (s ⁻¹)		J (s ⁻¹)
O ₃ → O(¹ D)	4.7×10 ⁻⁷	H ₂ O ₂	2×10 ⁻⁶	C ₂ H ₅ OOH	1.2×10 ⁻⁶
BrO	1.4×10 ⁻²	NO ₂	3.5×10 ⁻³	Cl ₂	8.5×10 ⁻⁴
Br ₂	2.1×10 ⁻²	NO ₃ → NO ₂ + O	1.4×10 ⁻¹	ClO	5.0×10 ⁻⁷
		→ NO + O ₂	1.7×10 ⁻²		
BrONO ₂	3.4×10 ⁻⁴	HNO ₃	4.4×10 ⁻⁸	HOCl	8.6×10 ⁻⁵
HOBr	3.0×10 ⁻⁴	HCHO → CO + H ₂	9.6×10 ⁻⁶	ClONO ₂	1.3×10 ⁻²
		→ CHO + H	5.5×10 ⁻⁶		
BrCl	5.7×10 ⁻³	CH ₃ CHO	6.9×10 ⁻⁷	OCIO	3.6×10 ⁻²
BrNO ₂	9.3×10 ⁻⁵	CH ₃ OOH	1.2×10 ⁻⁶		

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Table 6. Initial mixing ratios of base run of the model.

Species	[X] ₀	Species	[X] ₀	Species	[X] ₀
O ₃	40 ppb	CO	132 ppb	C ₂ H ₂	600 ppt
Br ₂	0.3 ppt	HCHO	100 ppt	C ₃ H ₈	1.2 ppb
Cl ₂	0.3 ppt	CH ₃ CHO	100 ppt	NO	5 ppt
CH ₄	1.9 ppm	C ₂ H ₆	2.5 ppb	NO ₂	10 ppt
CO ₂	371 ppm	C ₂ H ₄	100 ppt		

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Table 7. Factors related boundary layer Br-release and ozone depletion events.

Season	O ₃ -depletion	Light	Inversion
Winter	no	no	strong
Spring	yes	yes	yes
Summer	no	yes	no
Fall	no?	yes	weak

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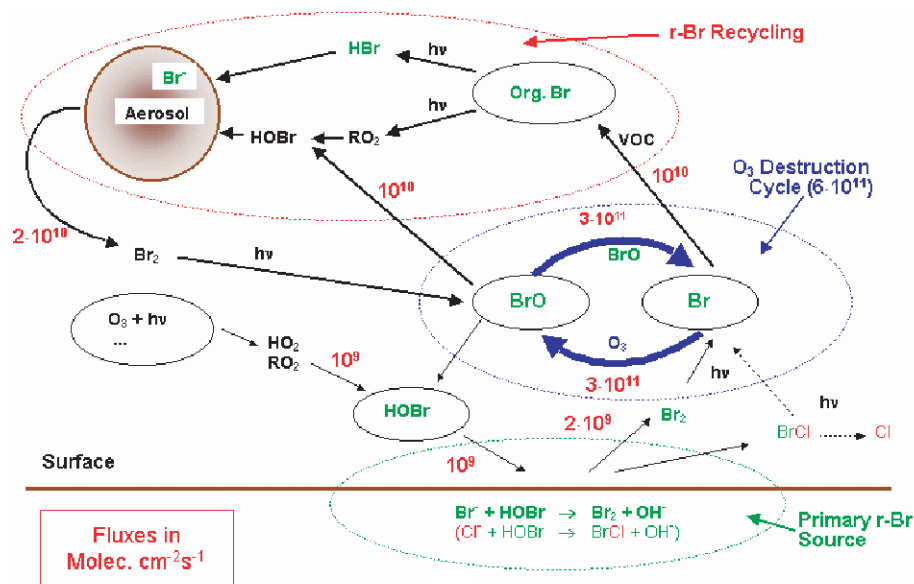


Fig. 1. Scheme of bromine explosion with neglected chlorine chemistry. See text for details. The thickness of the black arrows indicate the Br_x fluxes.

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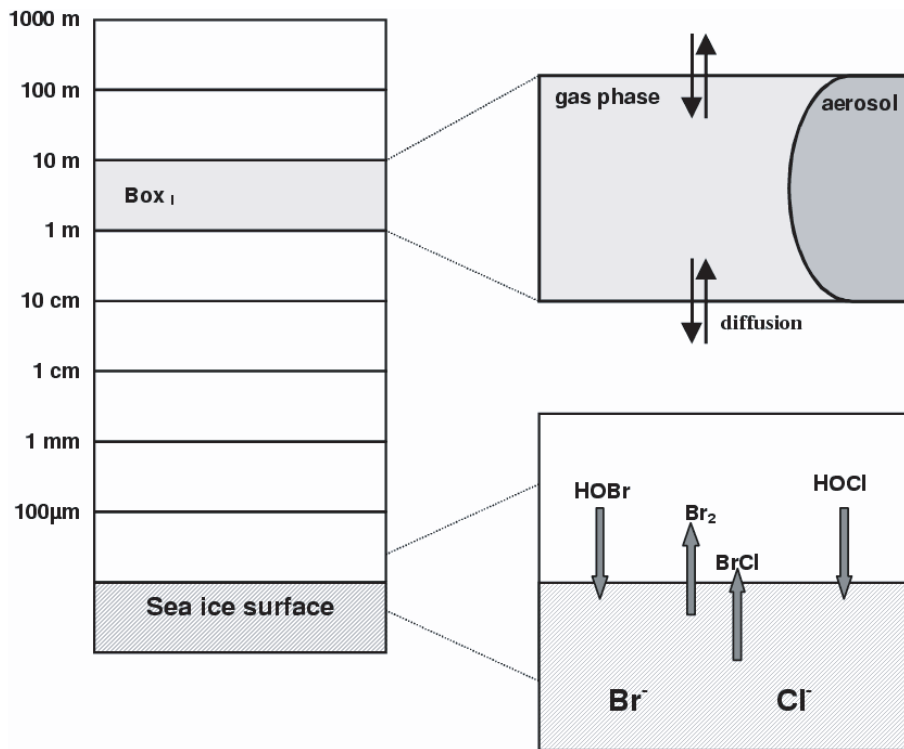


Fig. 2. Vertical structure of the model as used for the model calculations.

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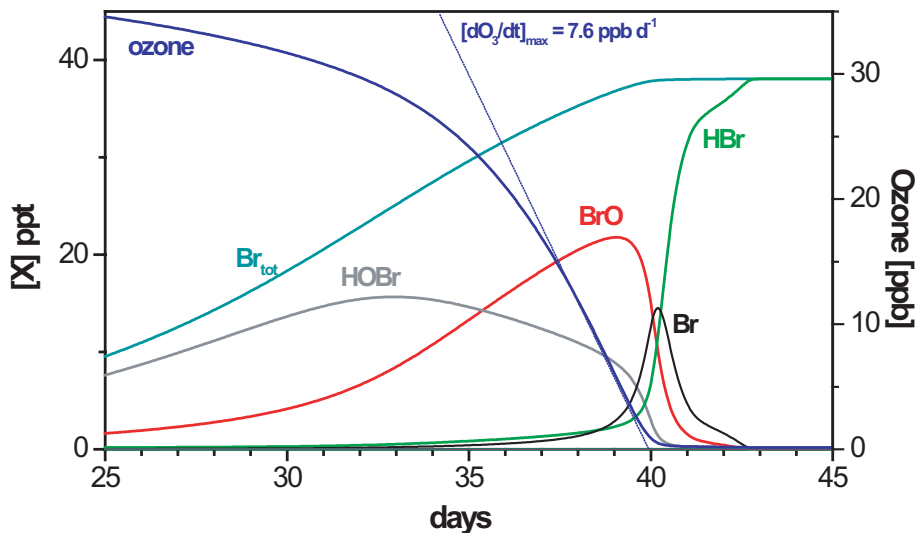


Fig. 3. Basic run (initially 0.6 ppt of Br and Cl; SZA fixed at 80°) – time series (day 25–day 45) of bromine species and ozone inside the top box (100–1000 m).

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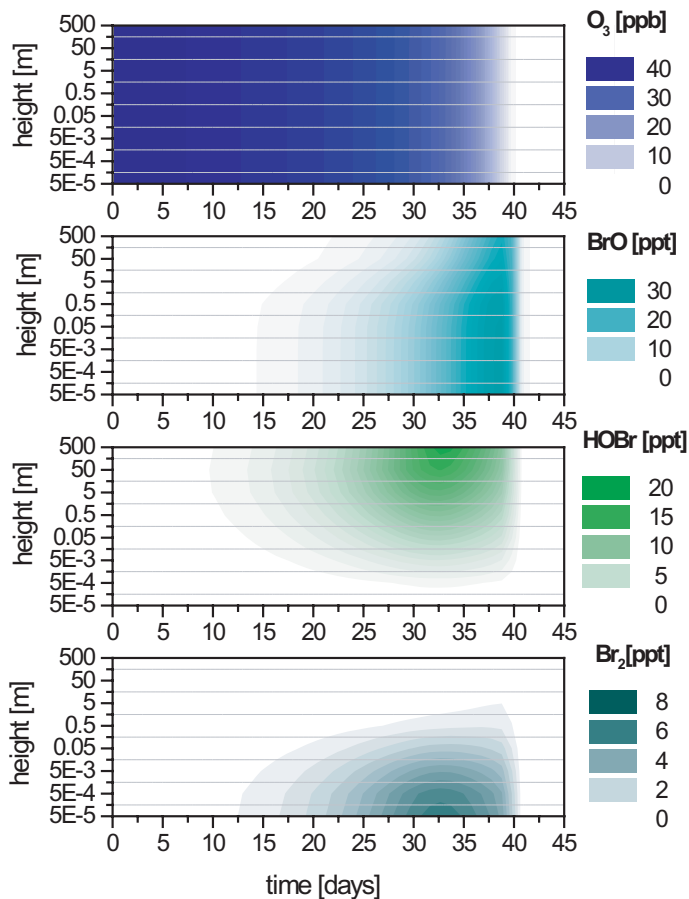


Fig. 4. Vertical concentration profiles for ozone and bromine species, according to simulation model basic run.

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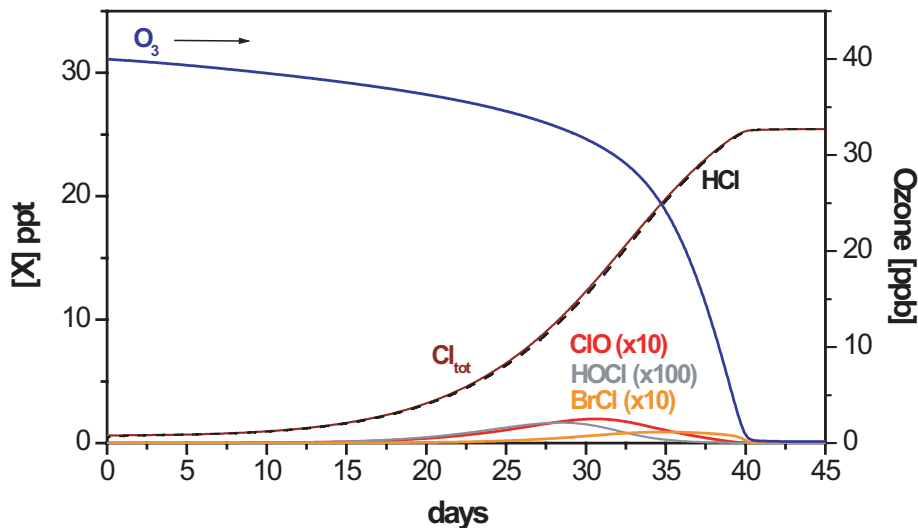


Fig. 5. Basic run (initially 0.6 ppt of Br and Cl; SZA fixed at 80°) – time series (day 25–day 45) of chlorine species and ozone inside the top box (100–1000 m).

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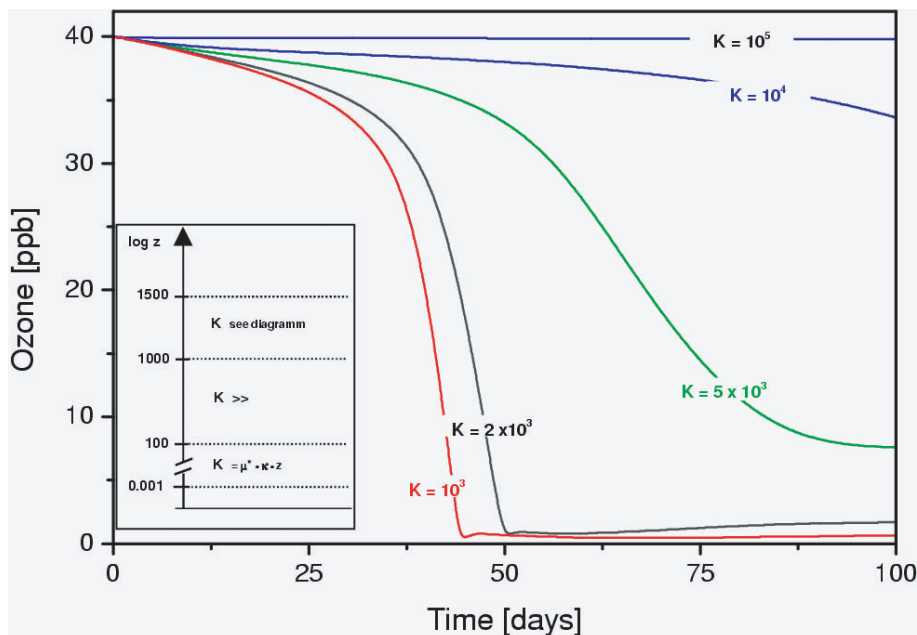


Fig. 6. Model results of ozone time series in the top box (100–1000 m) including turbulent diffusion of ozone of various strengths from the free troposphere into the boundary layer (see insert).

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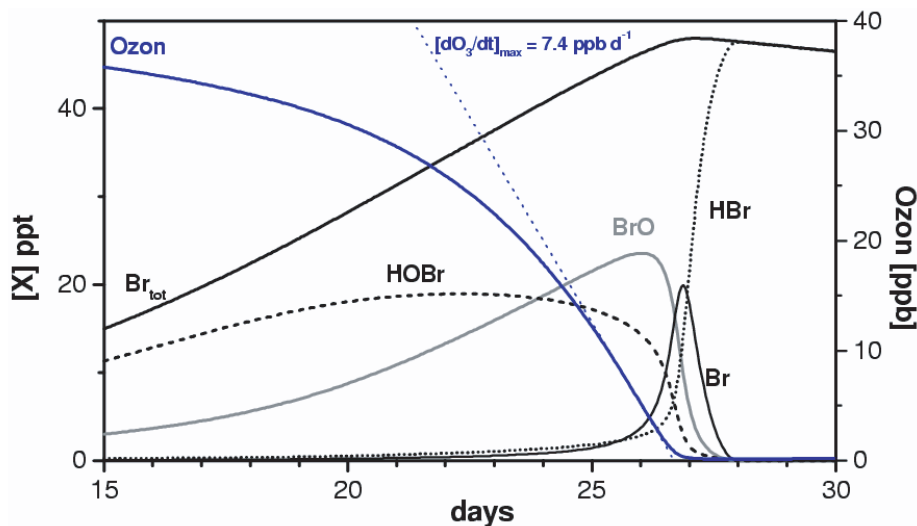


Fig. 7. Model run under the assumption of an additional halogen release out of sea salt aerosol (initially 0.6 ppt of Br and Cl; SZA fixed at 80°) – time series (day 15–day 30) of bromine species and ozone inside the top box (100–1000 m).

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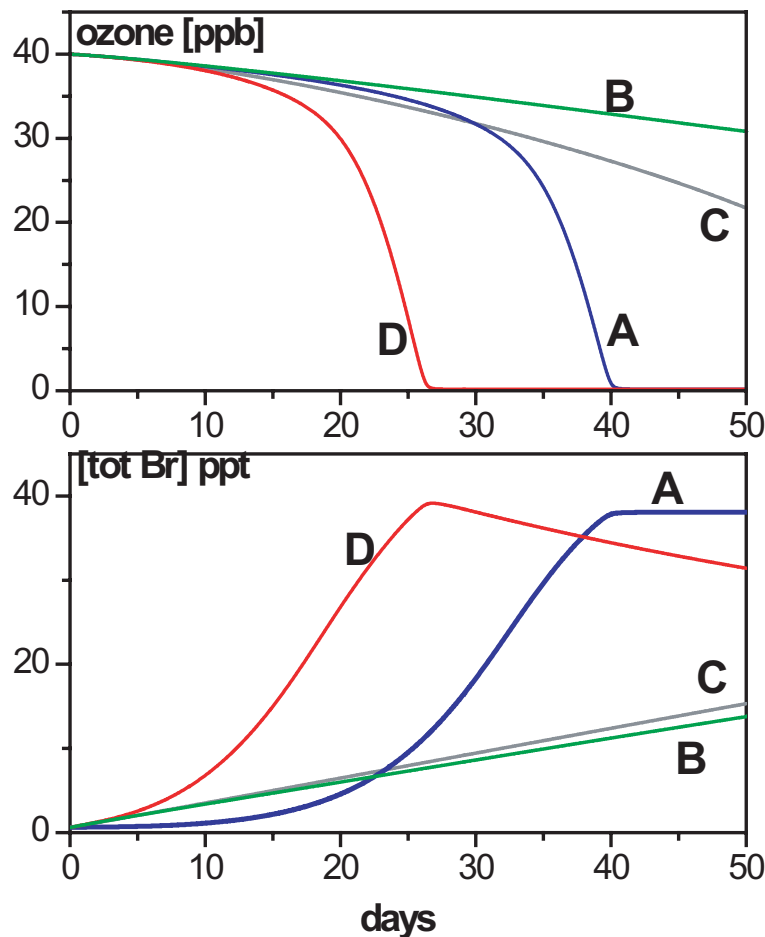


Fig. 8. Comparison of ozone record and the concentration of total bromine under different simulation conditions (A: only surface source; B: no halogen recycling at aerosol surfaces; C: only aerosol source; D: surface plus aerosol source).

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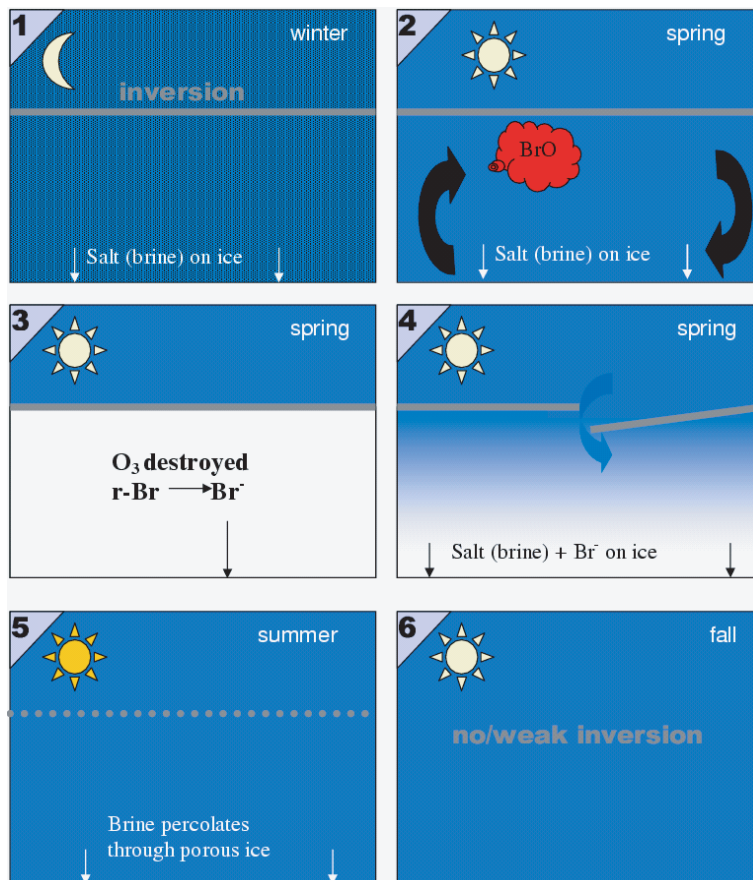


Fig. 9. Seasonal changes of the factors influencing bromine explosions and ozone depletion events. Only in spring all prerequisites are fulfilled (panel 3). See text for details.

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